京都大学学術情報リポジトリ
KURENAI 紅
Kyoto University Research Information Repository

京都大学
KYOTO UNIVERSITY

Title	Studies on explosion reaction : the reaction between carbon monoxide and oxygen I
Author(s)	Jono, Wasaburo
Citation	The Review of Physical Chemistry of Japan (1941), 15(1): 17-30
Issue Date	1941-04-30
URL	http://hdl.handle.net/2433/46583
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Kyoto University

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

STUDIES ON EXPLOSION REACTION. THE REACTION BETWEEN CARBON MONOXIDE AND OXYGEN. I.

By Wasaburo Jono.

Introduction

It is well known that the reaction between carbon monoxide and oxygen is an explosion reaction like the knall gas reaction, being of the chain type. The mechanism of this reaction will, therefore, be elucidated by examining the change of the reaction velocity with time immediately aftar the start of reaction. By the method of thermal analysis the present author[1] has investigated the initial stage of the reaction between hydrogen and oxygen and found this method advantageous for making clear the mechanism of the explosion reaction. Therefore, he now intends to apply the method to the oxidation of carbon monoxide with a view to elucidating its mechanism.

The oxidation of carbon monoxide, beside the knall gas reaction, is apparently the simplest reaction among explosion reactions and forms a common subject of inquiry pursued by many investigators. Its mechanism, however, is more uncertain than that of the knall gass reaction, and Sagulin[2], Semenoff[3], Garner[4] and others found the presence of two critical pressures — upper and lower — marking the explosion regions at a certain temperature. Though these critical pressures have been much studied since then, no satisfactory explanation of the explosion peninsula is given on the basis of experimental evidences. This is partly due to the fact that the reaction is affected by various experimental conditions more readily than the knall gas reaction. For instance, the presence of 0.1 % nitrogen dioxide reduces the critical temperature of explosion by 200°C.[3]; the effect of such an innert gas as nitrogen is also remarkable[3]. Above all, the water vapour produces a marked effect on the reaction[5], so much so that it has once been regarded as indispensable for the reaction. Carbon dioxide, the reaction product, greatly retards the reaction: it has been admitted that slow introduction of the reactant gas into the

1) W. Jono, This Journal, 9, 1 (1935).
2) Sagulin, *Z. physik. Chem.*, **B**, 1, 275 (1928).
3) Sagulin, Kowalsky, Kopp and Semenoff, *Z. physik. Chem.*, **B**, 6, 307 (1930).
4) Garner and Gomm, *Trans. Farad. Soc.* 24, 470 (1928).
5) Hadman, Thompson and Hinshelwood, *Proc. Roy. Soc.*, **A**, 138, 297 (1932); 137, 87 (1932).

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

reaction vessel makes the explosion more difficult to break out[4]. The upper and lower limits of explosion are influenced by the dimension of the vessel used, the nature of the previous explosion, the presence of carbon dioxide, etc.,[3) 5) 6)] and not so much by the water vapour[5]. As for the reaction at the non-explosion region, the reaction velocity is extremely small under pressures below the lower limit and even in the neighbourhood of the lower limit it never rises markedly. On the other hand, under pressures above the upper limit the velocity is also small, the upper limit being not so sharp as in the case of the knall gas reaction. Semenoff[7] pointed out that a faint glow was observed even under the pressure a little above the upper limit. The mechanism of the reaction has been discussed by Haber[8], Semenoff[7], Hinshelwood[5] and other investigators from experimental results, and yet no unshakable conclusion has been drawn. Thus, many factors, such as the surface of the vessel, the foreign gases, the reaction products etc. affect the reaction between carbon monoxide and oxygen. Accordingly, reproducible experimental results are hard to obtain even with unwearied attention, and this leads to the difficulty of the consideration of the reaction mechanism.

The aim of the present work is to elucidate doubtful points in the oxidation of carbon monoxide by taking advantage of the study of the initial reaction.

Experimental

Method.

The apparatus used and the method adopted are the same as in the case of the union between hydrogen and oxygen. Calibration was made at each experiment in order to make clear the relation between the pressure change and the movement of the vibrator of the oscillograph used. By introducing air at a fixed moderate speed seperately into both sides of the mica membrane through a small capillary tube, the movement of the vibrator for the change of pressure was photographed on a film immediately after each experiment and the calibration curve thus obtained was used.

Materials.

Carbon monoxide and oxygen used were prepared as follows. Carbon monoxide prepared from formic acid by dehydration with phosphoric acid was passed over the Pt-asbestos heated at about 400°C. to remove a trace of the oxygen present,

---

6) Cosslett and Garner, *Trans. Farad. Soc.*, 26, 190 (1930).

7) Semenoff, *Chem. Rev.*, 6, 347 (1929).

8) Haber and Bonhoeffer, *Z. physik. Chem.*, 137, 263 (1928).

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

washed with KOH solution to remove CO_2, dried with concentrated sulphuric acid and phosphorus pentoxide, and stored in a gas reservoir. Oxygen obtained from a bomb was purified by passing over the Pt-asbestos heated at about 400°C., dried with phosphorus pentoxide and stored. Even during the storage, both gases were dried for a month with phosphorus pentoxide. In order to keep the effects of water vapour and other substances as constant as possible, the same materials were used throughout the whole experiments.

Analysis of the Reaction Curve and Calculation of the Reaction Velocity

The calculation of the reaction velocity from the reaction curve photographed on the film was made by the method of thermal analysis as in the case of the reaction between hydrogen and oxygen[1]. When the number of molecules is changed by the reaction, the change of pressure caused by that of the number of the molecules as well as that of the heat of reaction must be taken into consideration. Therefore, it is expressed in the calculation.

Let us suppose such a reaction as $A+B \rightarrow C$ for the sake of simplicity. If it is assumed that the reactant gas obeys the ideal gas law, we have

$$p_1 V_1 = nkT_1.$$

When V_1 denotes the unit volume (1 c.c) and ν_1 the number of molecules in 1 c.c., this becomes

$$p_1 = \nu_1 k T_1 \; ; \qquad (1)$$

being differentiated with respect to time t,

$$\frac{dp_1}{dt} = k\left\{\frac{d\nu_1}{dt} T_1 + \nu_1 \frac{dT_1}{dt}\right\}. \qquad (2)$$

Let ν, T and p represent the number of molecules, temperature and pressure of the reacting system at the beginning respectively. When each becomes ν_1, T_1 and p_1 because of the change of the number of molocules and the heat of reaction, suppose that the following relations hold:

$$p_1 = p + \Delta p,$$
$$T_1 = T + \Delta T,$$
$$\nu_1 = \nu + \Delta \nu,$$

then we have

$$p + \Delta p = (\nu + \Delta \nu) k (T + \Delta T),$$
$$\frac{d(\Delta p)}{dt} = k\left\{\frac{d(\Delta \nu)}{dt}(T + \Delta T) + (\nu + \Delta \nu)\frac{d(\Delta T)}{dt}\right\}. \quad (3)$$

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

Suppose, again, that dx molecules of C are formed per unit volume during time dt by the reaction. In this case, when the molar heat of the formation of C and the mean molecular heat of A and B are represented by Q and C_v respectively, dT_1, the rise of temperature during dt, is expressed by

$$dT_1=\frac{\frac{Q}{N}dx}{\frac{C_v}{N}\nu}=\frac{Q}{C_v}\frac{dx}{\nu}. \qquad (4)$$

But, if dT_1', the cooling during dt, is taken into account, the actual rise of temperature becomes

$$dT_1-dT_1'=\frac{Q}{C_v}\frac{dx}{\nu}-dT_1'. \qquad (5)$$

The velocity of cooling $-\frac{dT_1'}{dt}$ is the function of the difference between T_1, the temperature of the reaction system, and T, that of its surroundings.

$$-\frac{dT_1'}{dt}=-\frac{d(\Delta T)}{dt}=f(\Delta T). \qquad (6)$$

Hence,

$$dT_1-dT_1'=\frac{Q}{C_v}\frac{dx}{\nu}-f(\Delta T)\,dt.$$

When this actual rise of temperature (dT_1-dT_1') is substituted for $d(\Delta T)$ in equation (3), putting $T+\Delta T\fallingdotseq T$, $\nu+\Delta\nu\fallingdotseq\nu$, equation (3) becomes

$$\frac{d(\Delta p)}{dt}=k\left\{\frac{d(\Delta\nu)}{dt}T+\nu\left[\frac{Q}{C_v\nu}\frac{dx}{dt}-f(\Delta T)\right]\right\}. \qquad (7)$$

If the cooling velocity is supposed to be proportional to ΔT, we have

$$-\frac{d(\Delta T)}{dt}=f(\Delta T)=k\Delta T.$$

Hence,

$$\Delta T=\frac{1}{\nu k}\Delta p^*,$$

we have

$$-\frac{d(\Delta p)}{dt}=k\Delta p,$$

---

* As ν is changed by the reaction, this equation is, strictly speaking, not established. The variation of ν, however, can not be known unless the reaction velocity is measured. Therefore, the cooling velocity was approximately calculated from this equation, and, in practice, the value of Δp was used, which had been calibrated under the assumption that the pressure falls at the same rapidity as the velocity in a stationary state from $t=0$, if no heating occurs.

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

where k is the cooling constant. When $k\Delta p$ is substituted in equation (7), it becomes

$$\frac{d(\Delta p)}{dt}+k\Delta p=kT\frac{d(\Delta\nu)}{dt}+\frac{k\nu Q}{C_v}\frac{dx}{dt}. \qquad (8)$$

Let y represent the change in the number of molecules in the case when one molecule of C is formed from A and B, we have

$$d(\Delta\nu)=y dx.$$

Accordingly, equation (8) is

$$\frac{d(\Delta p)}{dt}+k\Delta p=ykT\frac{dx}{dt}+\frac{kQ}{C_v}\frac{dx}{dt}$$

$$=\left(ykT+\frac{kQ}{C_v}\right)\frac{dx}{dt},$$

at a constant temperature $$=(K_1+K_2)\frac{dx}{dt}=K\frac{dx}{dt}. \qquad (9)$$

At the initial stage of the reaction, however the concentration of C is practically zero, and so representing the mol fractions of A and B by a and b respectively, we have

$$K_2=\frac{kQ}{aC_{vA}+bC_{vB}},$$

$$K_1=ykT.$$

Now, the data necessary to the reaction, $CO+\frac{1}{2}O_2=CO_2$, are as follows:

$$Q=68 \text{ K cal},$$

$$y=-\frac{1}{2},$$

$$k=1.029\times10^{-19} \text{ cc.mm./degree},$$

and the molecular heats of oxygen and carbon monoxide are both

$$C_p=6.50+0.0010\,T.$$

Hence,

$$C_v=6.50+0.0010\,T-R.$$

Thus, K in the above equation is readily calculated, and hence the reaction velocity.

The Cooling Velocity

The measurement of the cooling velocity was made by the same method as in the reaction between hydrogen and oxygen[1]. The values of the cooling constant, k, calculated from the observed velocity of cooling at the experimental temperature 545°C. are given in Table I.

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

Table I

Cooling constant k for CO : O_2=3 : 1 mixture

(Temp. =545°C.)

Total Pressure mm. Hg	k deg./sec. per 1° difference
150	1.29
200	1.41
250	1.53
300	1.62
350	1.73
400	1.84
450	1.94
500	2.03
550	2.12

In comparison with the cooling velocities of hydrogen and oxygen it is seen that the cooling velocity of carbon monoxide is approximately inversely proportional to the square root of the molecular weight at the same temperature and pressure.

The Limiting Pressure of Explosion

To know the limiting pressure of explosion under the same condition as in the measurement of the reaction velocity, as in the case of the H_2-O_2 reaction,[1] the upper and the lower limiting pressures of explosion were observed as follows.

The reaction vessel used in the measurement of the reaction velocity was

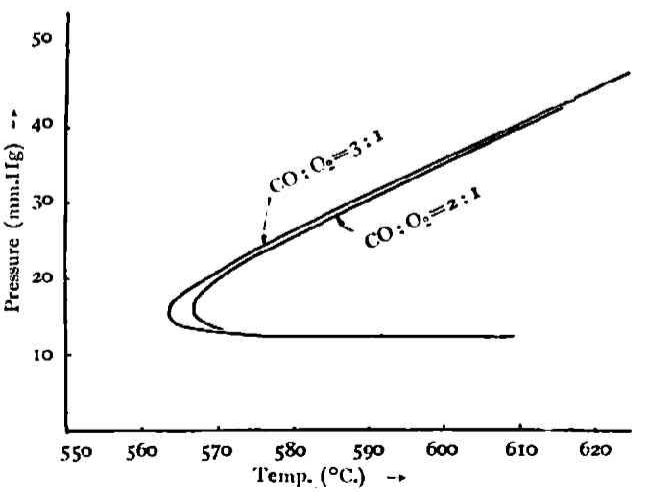


Fig. 1

Explosion limit of $CO+O_2$ mixture

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

made of Pyrex glass, but in this case a quartz vessel of the same dimension was used for high temperature measurement. The apparatus and the procedure were the same as in the reaction between hydrogen and oxygen. The result obtained is graphically shown in Fig. 1. As seen from the figure, the upper limit could be determined relatively accurately, but the lower limit was uncertain.

The Results of Experiments on the Reaction Velocity

The variation in the reaction velocity caused by the change of pressure is an interesting subject of research, and so a series of experiments were carried out under varying pressures with other conditions fixed. (Temperature=545°C.; $CO : O_2 = 3 : 1$). As shown in Fig. 1 the temperature of 545°C. is below the critical temperature of explosion. In the case when both gases are suddenly mixed, the expansion of the explosion region is far more remarkable than in the hydrogen-oxygen reaction, and even at 545°C. the upper limit is raised up to about 300 mm.Hg. Such expansion in the carbon monoxide-oxygen reaction as well as in the knall gas reaction may be ascribed to the absence of the retardation effect by the reaction product. If so, it is quite natural that such a large expansion as observed occurs, because CO_2 produces more marked effect upon the carbon monoxide-oxygen reaction than H_2O does upon the knall gas reaction. The upper limit varies a little according to the experimental conditions, but in the present experiment at 545°C. an explosion necessarily took place below 250 mm. The lower limit seems to be at 30—40 mm.Hg, though quite uncertain.

The Reaction Velocity near the Lower Limit

Table II and Fig. 2 show the velocity of the pressure change caused by the

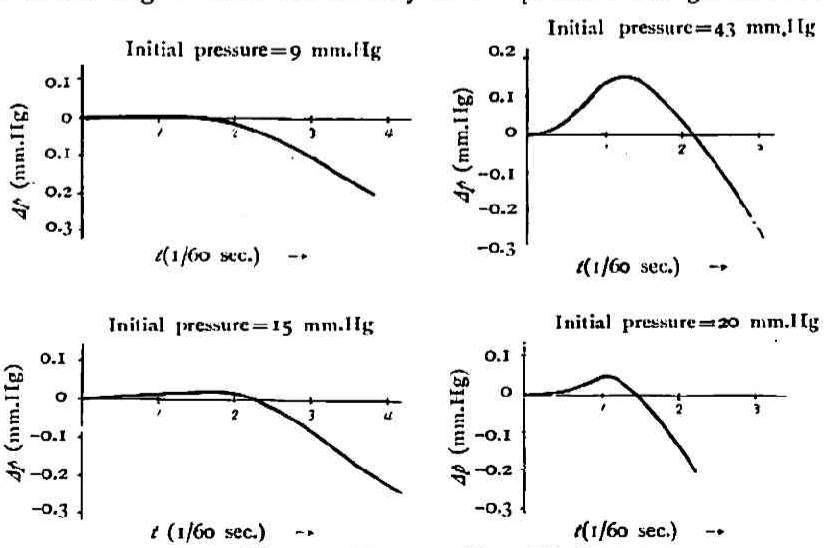


Fig. 2 Temp.=545°C. $CO : O_2 = 3 : 1$

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

Table II

Pressure Decrease due to the Reaction

Temp.=545°C. $CO : O_2 = 3 : 1$

Initial pressure=9 mm.Hg		Initial pressure=15mm.Hg	
t (1/60 sec.)	p (mm.Hg)	t(1/60 sec.)	p (mm.Hg)
0	0	0	0
0.75	0.006	0.25	0.
1.0	0.006	0.5	0.002
1.5	0.006	1.0	0.014
1.75	0.006	1.25	0.018
2.0	—0.012	1.5	0.014
2.5	—0.048	2.0	—0.019
3.0	—0.112	2.5	—0.079
4.0	—0.240	3.0	—0.150
		4.0	—0.270

Initial pressure=20 mm.Hg		Initial pressure=43 mm.Hg	
t (1/60 sec.)	p (mm.Hg)	t (1/60 sec.)	p (mm.Hg)
0	0	0	0
0.5	0	0.5	0.020
0.75	0.025	1.0	0.140
1.0	0.045	1.25	0.150
1.1	0.045	1.5	0.130
1.5	—0.012	2.0	0.025
2.0	—0.130	2.5	—0.090
2.5	—0.280	3.0	—0.240

reaction at low pressures. According to the prevailing opinion, the lower limit is the point where sudden change in reaction velocity—from a quite small value to infinite — occurs. The present experimental result, however, indicates the phenomenon similar to the case of the knall gas reaction[1]. What is considered to be the lower limit is a transitional zone, in which the reaction velocity varies from practically zero to infinite continuously and very rapidly though measurably. It is seen, therefore, that at about the lower limit the reaction in the non-explosion region and that in the explosion region are of the same nature.

The process of the reaction is similar to that of the knall gas reaction: the velocity is gradually accelerated from a very small initial value up to a maximum and then falls. If the time elapsing till the velocity reaches a maximum be called 'induction period', its duration is about 1/60 sec. It goes without saying that this 'induction period' thus named is different from the so-called induction period.

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

Though luminescence is observed in the reaction occuring at this region, increase in the pressure caused by the reaction heat is extremely small. Accordingly, the flame to be observed may be the cold flame.

The Reaction at the Explosion Region

There was hardly any induction period for the reaction of hydrogen and oxygen in its explosion region. On the contrary, in the explosion reaction between carbon monoxide and oxygen a considerably long induction period is observed in every case. The result obtained is given in Table III. The pressure change by the reaction is graphically shown in Fig. 3 and the change of the reaction velocity with time in Fig. 4.

These figures tell of the process of the reaction from its initiation to its explosion. Namely, the reaction velocity markedly rises shortly after the start of reaction and then falls — what is called degenerate explosion. Then a slight change of condition accelerates the reaction again and leads to true explosion. No quantitative relation was observed between the duration of the 'induction period' and the initial pressure. Consequently, this explosion seems to be caused by some unexpected change of condition, but this requires a further research. If the

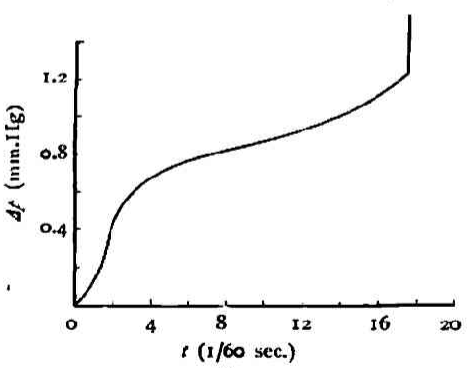


Fig. 3
Temp.=545°C $CO:O_2=3:1$
Initial pressure=360 mm.Hg

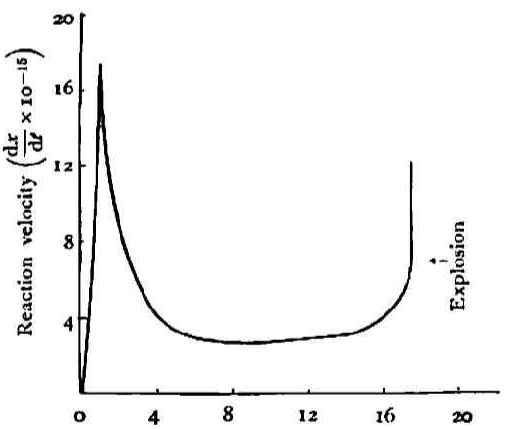


Fig. 4
Temp.=545°C. $CO:O_2=3:1$
Initial pressure=360 mm.Hg

maximum of the velocity which appears for the first time is so high as to cause self heating of the reaction system, the true explosion should break out at this time, and in fact the explosion of hydrogen and oxygen almost always took place at the first maximum; thus the 'induction period' could not be found. Of course, in the

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

case of the carbon monoxide-oxygen mixture, explosion of this kind also takes place, mainly under relatively low pressures.

Table III

Pressure Change and Reaction Velocity during the Induction Period of Explosion.

Temp.=545°C. $CO : O_2 = 3 : 1$

Initial pressure=360 mm.Hg

t (1/60 sec.)	p (mm.Hg)	$\frac{dx}{dt} \cdot 10^{-15}$
0	0	0
0.5	0.05	6.75
1	0.18	17.40
2	0.45	9.02
3	0.58	5.53
4	0.65	3.93
5	0.69	3.23
6	0.72	3.23
7	0.76	
8	0.78	2.59
10	0.81	2.68
12	0.87	2.94
14	0.93	3.12
15	0.96	3.47
16	0.98	4.02
17	1.01	4.93
17.5	1.06	6.48
		Explosion

The Reaction Velocity at Pressures above the Upper Limit

The results obtained with a mixture of CO and O_2 (3 : 1) at 545°C. are given in Table IV.

Table IV

Pressure Change and Reaction Velocity at Higher Pressures.

Temp.=545°C. $CO : O_2 = 3 : 1$

(1) Initial pressure=293 mm.Hg

t (1/60 sec.)	p (mm.Hg)	$\frac{dx}{dt} \cdot 10^{-15}$
0	0	0
1	0.05	3.67
2	0.19	5.88
2.5		10.54
3	0.31	5.05

(2) Initial pressure=360 mm.Hg

t (1/60 sec.)	p (mm.Hg)	$\frac{dx}{dt} \cdot 10^{-15}$
0	0	0
1	0.04	3.38
2	0.19	6.89
2.4		10.20
3	0.30	5.37

4	0.38	2.73
5	0.41	1.90
6	0.42	1.43
8	0.40	1.28
10	0.40	1.22
15	0.39	1.20
20	0.39	1.21

4	0.37	3.99
5	0.44	2.71
7	0.49	1.87
10	0.50	1.57
15	0.52	1.53
20	0.53	1.55

(3) Initial pressure=455 mm.Hg

t (1/60 sec.)	p (mm.Hg)	$\frac{dx}{dt} \cdot 10^{-15}$
0	0	0
1	0.07	4.95
1.6		8.27
2	0.23	7.20
3	0.33	4.09
4	0.39	2.95
5	0.42	2.31
7	0.45	1.74
10	0.47	1.37
15	0.47	1.28
20	0.48	1.27

(4) Initial pressure=520 mm.Hg

t (1/60 sec.)	p (mm.Hg)	$\frac{dx}{dt} \cdot 10^{-15}$
0	0	0
1	0.09	6.43
1.4		7.71
2	0.24	5.54
3	0.32	3.77
4	0.37	2.83
5	0.41	2.55
7	0.47	2.25
10	0.53	1.76
15	0.54	1.43
20	0.55	1.31

The pressure change of Table IV with zero point correction is shown in Fig. 5, and the relation between the reaction velocity calculated from Fig. 5 and time

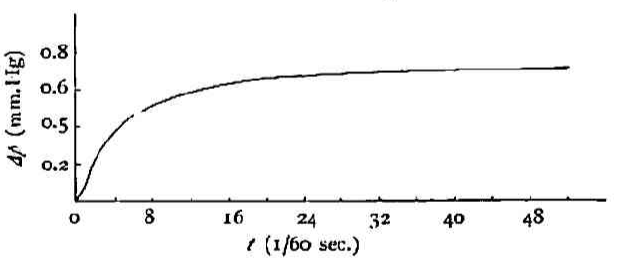


Fig. 5 a
Temp.=545°C. $CO : O_2 = 3 : 1$
Initial pressure=520 mm.Hg

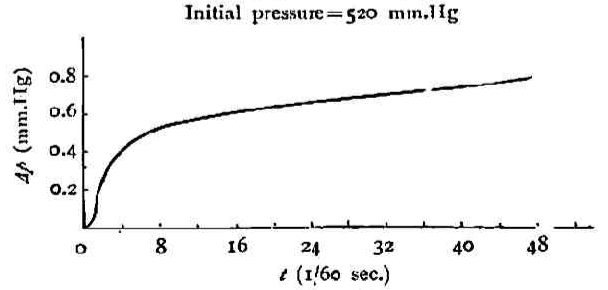


Fig. 5 b
Temp.=545°C. $CO : O_2 = 3 : 1$
Initial pressure=455 mm.Hg

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

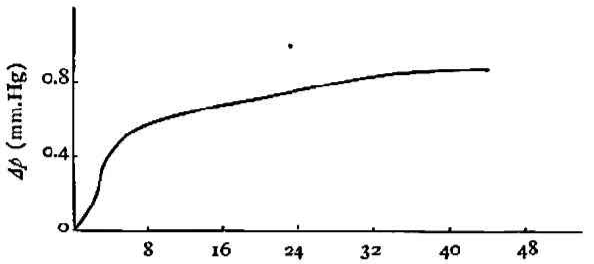


Fig. 5 c
Temp.=545°C. CO : O_2=3 : 1
Initial pressure=360 mm.Hg

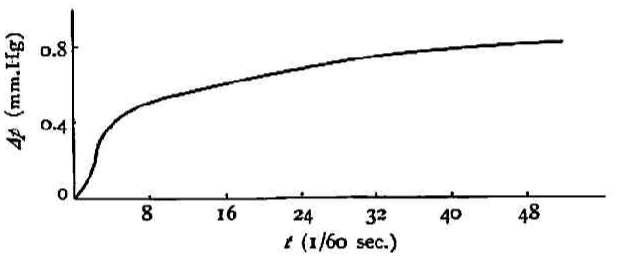
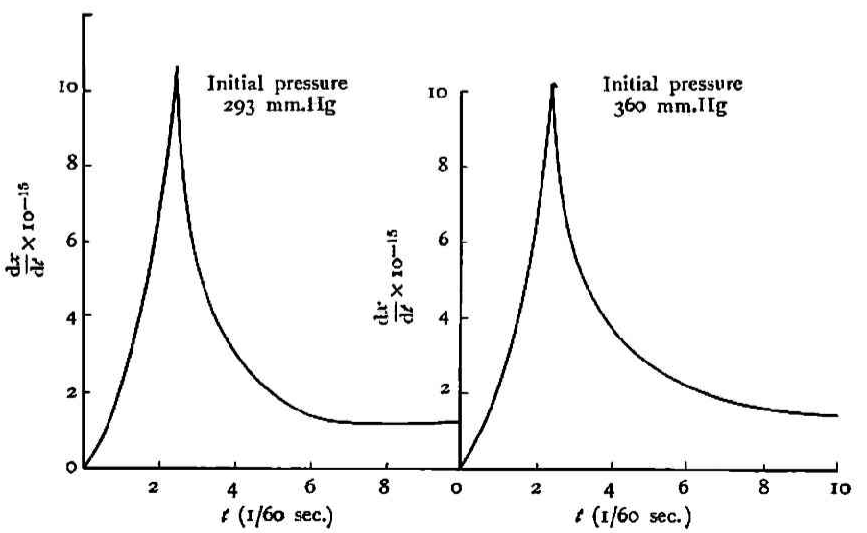


Fig. 5 d
Temp.=545°C. CO : O_2=3 : 1
Initial pressure=293 mm.Hg

is shown in Fig. 6 and in the third column of Table IV. As seen from Fig. 6, in any case, the reaction velocity, which is first low, reaches a maximum and then is reduced to a lower constant value which corresponds to the stationary state. There holds the following relation between the change of the reaction velocity with time and the initial pressure. The lower pressure is, i. e. the more approximate



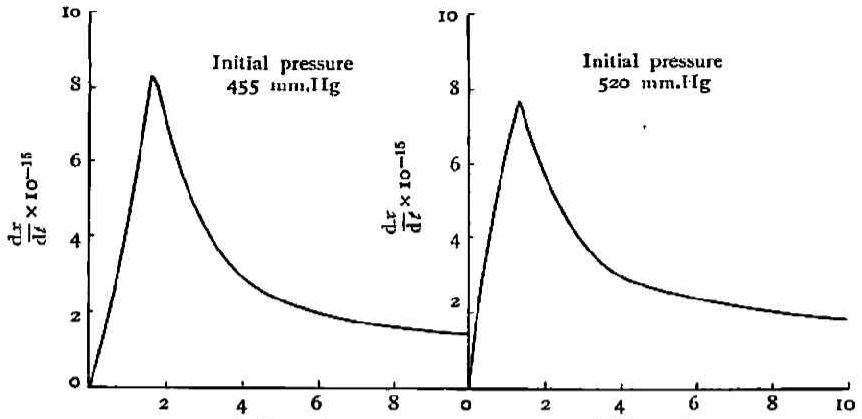


Fig. 6 Temp.=545°C. $CO : O_2 = 3 : 1$

it is to the upper limit, the higher the maximum velocity is. And the higher the pressure is, the shorter the time taken to reach a maximum velocity is. The lower the pressure is, the more rapid the fall of the velocity from a maximum is. In short, the higher the pressure is, the larger the velocity of the primary reaction is, and according as the pressure is raised, the type of the maximum becomes flat. Faint luminescence observed by Semenoff in the reaction occuring little above the upper limit seems to be the luminescence caused by the reaction of the maximum velocity when it is so large. This degenerate explosion, when its velocity becomes exceedingly high, is to bring forth true explosion and, therefore, it is inferred that the explosion taking place under a pressure belonging to the ordinary explosion range is due to the same mechanism as in the case of the knall gas.

Consideration of the Experimental Results

From the experimental results described above it is concluded that the oxidation of carbon monoxide resembles the knall gas reaction in many respects and that the characteristics of these reactions seems common to general oxidation reactions. That there is no discontinuous jump from the non-explosion to the explosion regions and that the reactions in both regions occur according to the same mechanism* are assumed from continuous change of the reaction velocity from zero to infinite at the lower limit and from the relation between violence of degenerate explosion and pressure near the upper limit as in the case of the reaction between hydrogen and oxygen. Moreover, it is also clear from the initial phenomenon of the explosion having the induction period.

* Such is not the case, of course, when self-heating of the reaction system does not keep the reaction isothermal, but it is the secondary effect.

The Review of Physical Chemistry of Japan Vol. 15f No. 1 (1941)

A sudden mixing of both gases leads to the expansion of the explosion region. The first question to be propounded for this fact is this: Does the explosion occur because of changed conditions, e. g. the ratio of mixture, as the gases are not uniformly mixed at the instant of mixing? In the present experiment, contrary to the reaction between hydrogen and oxygen, the experimental temperature 545°C. is the one below the critical temperature in the ordinary sense (see Fig. 1) and belongs to the range where explosion never occurs whatever the pressure or composition may be. Therefore, this question need not be taken into consideration. The second question is: Does neither the shock caused by the break of the glass diaphragm nor the surface newly formed at this moment lead up to an explosion? This question will be solved with the following experimental result. Under the present experimental condition a sudden mixing necessarily causes an explosion at 200 mm.Hg, but when 20 mm.Hg of CO is preliminarily added to oxygen, explosion never occurs. Therefore, the outbreak of explosion must be ascribed to either the absence of the retardation by the reaction products or the promotion of deactivation by the intermediate products.

The phenomenon of the peninsula of explosion can be rationally explained from the same mechanism as the reaction between hydrogen and oxygen. Namely, the lower pressure limit is assumed to be favorably brought forth by the action of the vessel wall and the upper pressure limit by mutual destruction of the intermediate products in the gaseous phase.

As the intermediate products in this assumption, either atoms or radicals are proposed. These products probably make and break the reaction chain by their mutual reaction.

This consideration somewhat suggests the scheme of the reaction. The examination of the reaction mechanism, however, will be more satisfactorily made after further studies have been performed under various experimental conditions and the confimation of intermediate products by the spectroscopic method have been made.

This work has partly been done at the Laboratory of Physical Chemistry of Kyoto Imperial University.

The author wishes to express his appreciation to Professor Horiba for his valuable suggestion throughout this work.

The Laboratory of Physical Chemistry,
Ryojun College of Engineering.

(Received December 2, 1940)